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(54) Title: Resin mouldings for optical applications

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Text of specifications

1. Title of the invention

Resin mouldings for optical applications

2. Claims

3. Detailed description of the invention

Field of industrial application

The present invention deals with resin mouldings for optical applications. In particular, it deals with optical element mouldings, such as the optical disc bases, lenses, prisms, etc.

Existing technology

Presently, playback methods where information recorded in very fine indentations with a spot laser on a disc are detected to play back images and sounds, and recording/ playback methods where the recording and playback of high density information is made possible by changing the optical properties of a recording layer on the surface of the disc are drawing much attention. The disc bases used in such recording and playback systems are required to have certain properties, such as

dimensional stability, optical uniformity, and small birefringence, in addition to transparency.

The use of resins for the disc base makes it possible to produce a large number of copies inexpensively. But it is well-known that molecular orientation usually occurs at the time of fluidising and cooling of the resin during the moulding of the disc base, resulting in the development of birefringence. This is a fatal defect. Molecular orientation during moulding is unavoidable, particularly in injection moulding. Currently, polymers consisting mainly of methyl methacrylate are the only resin materials with low optical anisotropy suited for making optical disc bases.

When conventional polymers consisting mainly of methyl methacrylate are used for making the disc base however, the dimensional stability is unsatisfactory because of the high hygroscopicity of the material, and the discs get warped in humid environments.

This problem has been discussed in detail, for instance, in Nikkei Electronics (page 133, June 7th issue, 1982). Therefore, aromatic polycarbonate resins, which have low humidity absorption, are now being used for making compact audio discs.

Aromatic polycarbonates have a highly anisotropic aromatic ring in its main chain, which makes it very difficult to reduce the birefringence of the moulded disc bases. Many attempts are being made to reduce the molecular weight and to find better moulding conditions. But, because the birefringence comes from the material itself, it is difficult to produce disc bases with uniformly low birefringence in a stable manner. It has been very difficult to produce, by injection moulding, discs with low birefringence that are larger in diameter than audio compact discs. Apart from this, there have been various attempts to improve the low dimensional stability of polymers consisting mainly of methyl methacrylate, which is their major drawback. Tokkaisho (Unexamined Japanese patent publication number Showa) 57-33446, 57-162135 and 58-88843 suggest the use of a copolymer of methyl methacrylate and an aromatic vinyl monomer.

However, copolymers with vinyl monomers having aromatic rings are very prone to development of large birefringence and are of not much practical value.

Even better control of birefringence and better dimensional stability are required in bases of discs that are not only used for playing back information but also for recording. However, resin materials that can sufficiently meet all these requirements have not been discovered so far.

Methacrylic resins have been traditionally used for optical elements like lenses and prisms also. But resin materials with even lower birefringence, better heat resistance, mechanical strength and dimensional stability are being demanded.

US patent 4,373,065 describes an optical recording element made of an optically isotropic resin with practically zero birefringence. This is achieved by mixing two types of completely miscible polymers having just the opposite optical anisotropy at a ratio that exactly cancels out the optical anisotropy of each polymer. This US patent also showed that in a system where polyphenylene and polystyrene are used as the polymers with the opposite optical anisotropy, if the composition of the mixture where the anisotropies are exactly cancelled out is used to make a film, the film does not develop birefringence even when stressed. In other words, such a polymer composition in the solid state does not acquire birefringence even when stress is applied.

Problems to be solved by the invention

The above-referred US patent 4,373,065, however, does not claim that if a polymer having this composition were made into optical disc bases by injection moulding, such optical materials would have very low birefringence. The present inventors therefore prepared optical elements, such as optical disc bases, using the modern method of injection moulding with a mixture of two types of completely miscible polymers that had exactly opposite optical anisotropy in the solid state, at a mixing ratio that would exactly cancel out the optical anisotropy of the two polymers, and found out that the birefringence of the injection moulded product was not always low.

In other words, when making optical materials such as optical disc bases from polymer compositions by injection moulding, it is not possible to obtain materials with low birefringence by simply using a composition that takes care of the optical anisotropy of the individual polymers in the solid state.

In recent years, there have been attempts to produce plastic bases for magneto-optical discs that can be erased and re-written.

For reading the information recorded on such magneto-optical systems, a polarised laser beam is focussed on the recording medium with the help of a lens and the slight rotation of the polarised light in the reflected laser beam because of the Kar effect is detected. Therefore, we have to use an optical disc base that does not easily add birefringence to incident light that comes in a diagonal direction.

While writing on such discs, the medium gets heated by the laser beam. So, the optical disc base must have high heat resistance.

Moreover, for resistance to various environmental factors, the recording medium and the optical base must have good adhesion for a long time.

Against the above background, the present invention aims at providing resin mouldings for optical applications, with various advantageous properties. These include low birefringence when injection moulded or compression moulded, with the mouldings giving low birefringence even to incident light coming in from a diagonal direction, high heat resistance, good balance of mechanical properties, good dimensional stability, and good adhesion with the recording medium for a long time.

The solution

The present invention deals with a resin composition for optical applications, that comprises of 30-70 wt.% of a copolymer consisting mainly of units of an aromatic vinyl monomer and a carboxylic acid group-containing vinyl monomer units, and 70-30 wt.% of a polyphenylene ether.

In the new invention, "aromatic vinyl monomer unit" means, for instance, styrene, α -methyl styrene, m-methyl styrene, p-methyl styrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, m-bromostyrene and p-bromostyrene. Among these, styrene is particularly suitable.

The "carboxylic acid group-containing vinyl monomer unit" can, for instance, be methacrylic acid, acrylic acid, crotonic acid, maleic acid, fumaric acid and itaconic acid. Among these, methacrylic acid is particularly suitable.

The suitable proportion of aromatic vinyl monomer in the copolymer with the carboxylic acid group-containing monomer is 80-99 wt.%. With less than 80% of aromatic vinyl monomer, the hygroscopicity of the resin obtained would be too high.

The amount of the carboxylic acid group-containing vinyl monomer in the copolymer is 1-20 wt.%. With less than 1 wt.% of this component, the characteristic features arising from the carboxylic acid group will not manifest sufficiently.

Apart from these components, a copolymerisable vinyl monomer can also be mixed in the composition. But its type and amount must be suitably selected, taking into account the transparency and hygroscopicity of the resin material.

The above-mentioned copolymer should have a melt flow rate (MFR) of 0.5-200 at 230°C under 3.8 kg load. The preferable MFR is 2-100. An MFR of more than 200 is not desirable because this would adversely affect the mechanical strength of the material. Less than 0.5 is also not suitable because this makes it difficult to lower the birefringence.

The copolymer consisting of the aromatic vinyl monomer and the carboxylic acid group-containing vinyl monomer can be prepared by bulk polymerisation, suspension polymerisation, emulsion polymerisation or solution polymerisation, using a radical initiator. However, bulk or suspension polymerisation is preferable considering the productivity and the need to prevent intermixing of impurities.

Examples of radical initiators that can be used are peroxides like lauroyl peroxide, benzoyl peroxide, di-*tert*-butyl peroxide, dicumyl peroxide, etc and azo compounds like 2,2'-azobis isobutyronitrile and 1,1'-azobis(1-cyclohexane carbonitrile).

In addition to this, for regulating the molecular weight, a chain transfer agent like *tert*-butyl, *n*-butyl, *n*-octyl, *n*-dodecyl and tertiary dodecyl mercaptans may be added if needed. The polymerisation may be normally carried out in the temperature range 50-150°C.

"Polyphenylene ether" in this invention means a polymer with repeating units that can be represented by the general formula given below.

(Here, R^1 to R^4 are hydrogens, halogens or hydrocarbon groups)

Such polyphenylene ethers are polymers prepared by oxidative coupling of phenol monomers. They can be easily prepared by a well-known method where a copper or a manganese catalyst is used (like the methods described in Japanese patents 36-18692 and 47-36518).

Practical examples of such polyphenylene ethers are poly(2,6-dimethyl-1,4-phenylene)ether, poly(2-methyl-6-ethyl-1,4-phenylene)ether, poly(2-methyl-6-propyl-1,4-phenylene)ether, poly(2,6-dipropyl-1,4-phenylene)ether, poly(2-methyl-6-bromo-1,4-phenylene)ether, etc. Among these, poly(2,6-dimethyl-1,4-phenylene)ether is particularly suitable.

The suitable range of mean molecular weight of the polyphenylene ether is 0.1-1.0, preferably 0.3-0.7, expressed in terms of the limiting viscosity (in chloroform, measured at 25°C). If this viscosity is less than 0.1, the resin mouldings for optical applications prepared from it would not have a sufficiently low birefringence and its

strength would not be good enough. Also, if it is larger than 1.0, the resin mouldings would not have good uniformity, besides having a melt flow rate that is too low.

The resin used in the new invention is prepared by mixing a copolymer containing an aromatic vinyl monomer and a carboxylic acid group-containing vinyl monomer and a polyphenylene ether. Melt-mixing and solution mixing are suitable for this mixing.

Melt-mixing may be done under a high shearing force in a mixing device such as an extruder, Banbury mixer, kneader blender, heated rollers, etc.

The mixing must be done to the extent that both the polymers are dispersed to units of $1\ \mu$ or less. Preferably, the mixing may be continued up to a state of molecular level mixing. Whether molecular level mixing has been achieved or not can be easily found out by checking whether the glass transition point of the mixture has become one single value.

To achieve thorough and satisfactory mixing, a higher mixing temperature, a longer mixing time, or a higher shearing force, etc may be employed.

In melt-mixing, a small amount of organic solvent may be added as a plasticiser to make the mixing easier by lowering the melting temperature of the polymers. The organic solvents listed for use in solution mixing are applicable here also. After the mixing, this organic solvent may be evaporated off.

In solution mixing, the polymers are dissolved in an organic solvent to prepare a solution of at least 1 wt.%. Then, after obtaining a uniform mixture through stirring and blending, the organic solvent may be evaporated off. Alternatively, a poor solvent of the two polymer components may be added to the uniform mixture prepared, to allow the precipitation of the polymer mixture.

Examples of suitable organic solvents are chloroform, methylene chloride, ethylene chloride, toluene, benzene and chlorobenzene. Examples of poor solvents are methanol, ethanol, propyl alcohol, n-hexane and n-pentane.

The mixing ratio of the copolymer component, consisting of the aromatic vinyl monomer and the carboxylic acid group-containing vinyl monomer, and the polyphenylene ether should be 30-70, preferably 40-55 wt.% of the former and 70-30, preferably 60-45 wt% of the latter.

If the polyphenylene ether component is less than 30 wt.% or more than 70 wt.%, the resin mouldings would not have a sufficiently low birefringence. With less than 30 wt.% of this component, the heat resistance is also not satisfactory.

In practice, the resin composition is decided suitably within the above-specified range, taking into account the moulding method employed.

For example, when employing injection moulding, the proportion of the polymer components may be suitably adjusted, depending on the moulding conditions selected, i.e., resin temperature, moulding pressure, mould temperature, etc, so that the birefringence of the mouldings obtained satisfy the performance requirements of their intended applications.

In the newly invented method, such resin mouldings can, for instance, be magneto-optical disc bases, various types of lenses and prisms, apart from ordinary optical disc bases. Among such resin mouldings, the optical disc bases permit the passage of light such as that of the semiconductor laser beam.

It should preferably have a light transmittance of 75% or better, in a material of thickness of 1.2 mm.

Injection moulding, compression moulding, injection-compression moulding, etc. may be employed for producing the newly invented resin mouldings for optical applications. The effect of the new invention will be more profound if a moulding that

normally causes high birefringence is employed. In this respect, and from the productivity point of view, injection moulding is most suitable.

Effectiveness of the invention

The newly invented resin mouldings for optical applications have low birefringence when produced by injection moulding or compression moulding, the birefringence being low even for incident light coming from a diagonal direction. Their heat resistance is high, the balance of mechanical strengths is good, and the dimensional stability is superior.

Besides this, when prepared as optical disc bases, the newly invented mouldings have good adhesion with the recording medium and superior environmental resistance. Therefore, we can say that the new invention has a very significant effect in reducing the cost and promoting versatile use of magneto-optical discs.

Examples

We shall now explain the new invention with the help of some practical examples.

In these examples both "parts" and "%" are given on weight basis. The physical properties and performance were evaluated by the methods described below.

.Limiting viscosity of the polymer

Measured in chloroform solvent at 25°C using a Ubbelohde viscometer and calculated.

.Water absorption

Equilibrium water absorption was measured in distilled water of 60°C, as per ASTM D-570.

.Light transmittance

Light transmittance was measured at 800 nm, with a 1.2 mm thick sample using an Autorecording Spectrophotometer 330 (Hitachi Ltd.).

.Bending property

Measured as per ASTM D-790.

.Heat resistance

Was expressed in terms of glass transition point of a 5 mm x 5 mm x 3 mm test piece, measured by the linear expansion coefficient method.

.Birefringence

Retardation was measured at 546 nm by the Sennermon compensator method, using a polarising microscope.

.Performance of the magneto-optical discs**. . Heat history conditions of the discs**

Relative humidity: Maintained constant at $93 \pm 3\%$

Temperature change: One cycle of 24 h

<u>Temperature (°C)</u>	<u>Duration (h)</u>
25	2.0
25-> -10	0.75
-10	2.75
-10 -> 25	0.5
25	1.0
25 -> 65	1.5
65	5.0
65 -> 25	1.5
25	1.0
25 -> 65	1.5
65	5.0
65 -> 25	1.5

. . Conditions of recording on the discs

rpm: 1,800

Recording frequency: 1 MHz (for C/N)

3 MHz (for BER)

Duty: 50%
Recording power: 6 mW
Recording magnetic field: 350 Oe
Recording time: 10 sec (for about 300 tracks)

.. C/N : Measured at the position of disc radius 30 mm using a magneto-optical disc evaluation device OMS-1000 (Nakamichi Co.).

.. Bit error rate (BER): Measured using the same evaluation device, at replay output 1 mW, measurement was made at disc radius 40, 45, 50, 55 mm and the mean value calculated.

.. Condition of recording layer: Examined visually

. Blending and pelletisation were done in a biaxial extruder (Tex 30-30BW-2V, Nihon Seiko Co. Ltd.)

. The extrusion moulding machine used was Neomat 150/75 (75 tonne, Sumitomo Heavy Industries Ltd) and a disc mould for 130 mm diameter and 1.2 mm thick mouldings was used.

Example 1

Following the method described in Example 2, No. 9 of Japanese Patent 47-86518, 2,6-xylylenol was polymerised using manganese chloride and ethanolamine as catalysts to obtain poly(2,6-dimethyl-1,4-phenylene)ether with limiting viscosity 0.50 (in chloroform, 25°C). 2640 ml of distilled water was placed in a 5 l capacity separable flask. To this was then added, 2.7 g of hydroxyethyl cellulose (suspension stabiliser) and dissolved. 1170 g of styrene, 130 g of methacrylic acid and 6.5 g of benzoyl peroxide were then added to the flask in that order. After purging the air inside the flask with nitrogen, the flask was heated under stirring at 500 rpm and the contents allowed to undergo suspension polymerisation for 4 h at 90°C. The reaction was allowed to continue for another hour at 98°C.

The granular resin formed was washed, dehydrated and dried to obtain about 1300 g of copolymer resin. The melt flow rate (MFR) of this resin at 230°C under 3.8 kg of load was 25 g/min.

The polyphenylene ether and the styrene-methacrylic acid copolymer prepared as described above were mixed at 60:40 ratio, kneaded and pelletised in an extruder.

Some of these pellets were used to determine light transmittance, water absorption, bending property and heat resistance. The results are given in Table 1.

The pellets were then injection moulded at cylinder temperature 320°C and mould temperature 85°C into grooved disc bases (groove pitch 1.6 μ), diameter 130 mm and thickness 1.2 mm.

The birefringence of these grooved disc bases was measured at a point 35 mm from the centre. The results are given in Table 1.

Reactive sputtering was applied to the disc bases prepared above under the reduced pressure of 5×10^{-3} Torr in an argon-nitrogen gas mixture to form an 850 Angstrom thick silicon nitride film with refractive index 2.0.

Then, a 900 Angstrom thick Tb Fe Co magnetic layer was deposited by the sputtering following the standard method. An 850 Angstrom thick silicon nitride layer was then made over the magnetic layer by the same method as mentioned earlier to prepare magneto-optical discs having a base/silicon nitride/Tb Fe Co/silicon nitride layer structure. The results of performance evaluation of these magneto-optical discs are given in Table 1.

Comparative Example 1

Following the method described in Example 2, No. 9 of Japanese Patent 47-86518, 2,6-xylylenol was polymerised using manganese chloride and ethanolamine as catalysts to obtain poly(2,6-dimethyl-1,4-phenylene)ether with limiting viscosity 0.40 (in chloroform, 25°C).

The polyphenylene ether prepared above and a polystyrene resin (Espride® 4-62A, MFR 24, Nihon Polystyrene Kogyo) were mixed at 50:50 ratio, kneaded and pelletised in an extruder, and processed as in Example 1. The results are given in Table 1.

Table 1

	Parameters evaluated			Example 1	Comparative example 1
Resin pellets	Light transmittance (%)			87	88
	Water absorption (%)			0.15	0.10
	Bending strength (kg/cm ²)			760	1060
	Heat resistance (°C)			162.1	146.8
Disc base	Birefringence (nm)			-2.0	+2.0
Magneto-optical disc	Heat history	Before	C/N (db)	46	46
			BER	8.1×10^{-5}	7.8×10^{-5}
			Condition of recording layer	_____	_____
		After one cycle	C/N (db)	46	46
			BER	8.1×10^{-5}	3.1×10^{-4}
			Condition of recording layer	No change	No change
		After 10 cycles	C/N (db)	46	45
			BER	8.1×10^{-5}	9.2×10^{-4}
			Condition of recording layer	No change	No change
		After 30	C/N (db)	45	40

		cycles	BER	8.2×10^{-5}	2.4×10^{-3}
			Condition of recording layer	No change	Bubbles developed

The rest of the source text is a formal application submitted by the applicant for correction of errors in the Text of Specifications. This has not been translated here. The corrections have been incorporated in the translated text - Translator

Transinfo notes:

- 1. Kindly check parts marked in orange. Their translation is uncertain or the original is not legible*
- 2. Parts where the source text appears to have errors are marked in pink.*